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Authors
Gaffney, JS
Marley, NA
Blake, DR

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Baseline measurements of ethene in 2002: Implications for increased ethanol use and biomass burning on air quality and ecosystems

Jeffrey S. Gaffney [a,*], Nancy A. Marley [a], Donald R. Blake [b]

[a] Department of Chemistry, University of Arkansas at Little Rock, Little Rock, AR 72044, USA
[b] Department of Chemistry, University of California, Irvine, CA 92697, USA

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ABSTRACT

While it is well known that combustion of ethanol as a biofuel will lead to enhanced emissions of methane, ethene (ethylene), acetaldehyde, formaldehyde, and oxides of nitrogen (primarily NO) when compared to gasoline alone, especially during cold starts or if catalytic converters are not operating properly, the impacts of increases in atmospheric ethene levels from combustion of fuels with higher ethanol content has not received much attention. Ethene is a well known and potent plant growth hormone and exposure to agricultural crops and natural vegetation results in yield reductions especially when combined with higher levels of PAN and ozone also expected from the increased use of ethanol/gasoline blends. We report here some baseline measurements of ethene obtained in 2002 in the southwestern and south central United States. These data indicate that current ethene background levels are less than 1 ppb. Anticipated increases in fuel ethanol content of E30 or greater is expected to lead to higher atmospheric levels of ethene on regional scales due to its atmospheric lifetime of 1.5–3 days. These background measurements are discussed in light of the potential enhancement of ethene levels expected from the anticipated increases in ethanol use as a renewable biofuel.

1. Introduction

With the realization that fossil fuels are not renewable and therefore are a limited resource, it is clear that renewable energy sources must continue to grow in importance if we are to develop a sustainable energy policy. Combustion of either fossil fuels or biofuels has impacts on the environment, particularly on air quality, which will need to be addressed in order to insure an environmentally friendly, sustainable energy economy (Gaffney and Marley, 2009). Ethanol, produced from corn and sugar cane, has developed into a renewable biofuel source that can be used as a gasoline replacement in internal combustion engines. It is usually offered as an ethanol-gasoline blend denoted as an ethanol additive at some percentage of ethanol. Thus, E10 is a mixture of 10% ethanol and 90% gasoline and E85 would be an 85% ethanol and 15% gasoline mixture. Currently E10–E15 gasoline blends are commonplace across the United States with some states moving towards the widespread use of E85.

The combustion of ethanol in internal combustion engines leads to the emission of methane, ethene (ethylene), acetaldehyde, formaldehyde, and higher oxides of nitrogen (primarily NO) compared to gasoline alone (Gaffney and Marley, 2009; Poulopoulos et al., 2001). These emissions can lead to the enhanced atmospheric production of ozone and peroxyacetyl nitrate (PAN) (Tanner et al., 1988; Jacobsen, 2007; Ginnebaugh et al., 2010; Pereira et al., 2004). For example, it is well established that the reaction of OH radicals with acetaldehyde will lead to the formation of PAN via the following reactions:

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O$$

$$CH_3CO + O_2 \rightarrow CH_3COO_2$$

$$CH_3COO_2 + NO_2 \leftrightarrow CH_3COO_2NO_2 (PAN)$$

PAN initially discovered via its observed ability to damage plants in Southern California is a potent phytotoxin (Gaffney and Marley, 2005). It is also a strong lachrymator as is its precursor acetaldehyde. Currently, controls on reactive hydrocarbon emissions have led to lower PAN levels in U.S. urban centers. However, increases in

* Corresponding author. Tel.: +1 501 569 8840; fax: +1 501 569 8838.
E-mail address: jsgaffney@ualr.edu (J.S. Gaffney).

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ethanol combustion are likely to lead to increased levels of acetaldehyde and nitrogen oxides (NO and NO_2) and, therefore, higher PAN levels (Jacobsen, 2007; Ginnebaugh et al., 2010).

The reactions of peroxy radicals with NO also lead to the formation of enhanced levels of ozone. Modeling studies of the anticipated use of very high ethanol fuel levels such as E85 have been shown to lead to higher ozone levels due to the higher NO emissions and photochemically active aldehyde emissions (Pereira et al., 2004; Ginnebaugh et al., 2010; Williams, 2004). Increases in both PAN and ozone levels are of concern due to their potential ability to impact plants, both natural and agricultural, leading to reduction of yields. PAN can also act to transport reactive nitrogen dioxide over larger distances thus leading to increases in regional ozone as well as the formation of peroxyacetic acid (CH_3COO_2H) in remote regions, where NO levels are low, through reaction of the peroxyacetyl radical with HO_2 radicals (Gaffney et al., 1989; Gaffney and Marley, 2005).

While it is well known that ethanol combustion will lead to enhanced ethene emissions, especially during cold starts or if catalytic converters are not operating properly, the impacts of increases in atmospheric ethene levels from combustion of fuels with higher ethanol content has not received much attention. Modeling efforts have indicated that ethene levels may be significantly higher if E85 use is widespread (Jacobsen, 2007; Ginnebaugh et al., 2010). Ethene is a well known and potent plant growth hormone and was originally noted as an air pollutant of concern due to its damaging effects on crops and horticulture (Burg and Burg, 1965; Ecker, 1995; Harvey, 1928; Stahl, 1969). Indeed, yield reductions of >50% have been found for ethene exposures to rice and wheat at levels of tens of ppb (Klassen and Bugbee, 2002).

Currently there is not a considerable amount of data available on what the regional background (baseline) ethene levels are in the U.S. This is likely due to the fact that current analytical methods used to measure volatile organic hydrocarbons have focused on the $>C_2$ hydrocarbons, or have looked at methane alone. As well, current measurement methods used for reactive hydrocarbons have sought to obtain rapid response analysis by using proton-transfer mass spectrometry (PTRMS). These methods, while very useful for the volatile organic compounds $>C_2$, do not determine ethene as it has the same mass number as molecular nitrogen and carbon monoxide. Background level ethene measurements require the use of canister sampling coupled with GC/FID analysis or absorption spectroscopic methods such as IR photoacoustic or high resolution long path FTIR spectroscopy, and these methodologies have not been routinely used. Past measurements of ethene range from the low ppt to high ppb, with levels in Los Angeles and Texas reaching the low ppm in the 1950–60s (Stahl, 1969). More recent measurements of ethene in the troposphere have been made at surface sites and from aircraft and have ranged from a few ppt to tens of ppb (e.g. Blake et al., 2003; Goldstein et al., 1996). Measurements of tropospheric ethene have been attempted on a large scale by using infrared solar occultation with satellite measurements of the Atmospheric Chemistry Experiment FT spectrometer (ACE-FTS, Herbin et al., 2009). The satellite results yield ethene data from 6 km and above, which indicate northern high latitude wintertime maximum ethene values above 50 ppt with some values at 200 ppt levels during 2005–2006 (Herbin et al., 2009). As ethene is ground sourced from both vegetative emissions and combustion, the ACE-FTS data aloft indicate that the boundary layer ethene concentrations should be significantly higher, due to its decrease by dilution and reaction before reaching 6 km and higher in the free troposphere.

We report here some baseline measurements of ethene obtained in 2002 in the southwestern and south central United States. Noting that in 2002 ethanol use was only 1% of the mobile fuel used nationwide and most of that use was in areas where ethanol addition to the gasoline was mandated as an air quality control strategy (U.S. Energy Information Energy, 2012), the canister based data presented here should serve as a reasonable regional baseline for the mid-southern U.S. for future evaluations of atmospheric ethene trends and for modeling of the impacts of increased use of ethanol as a gasoline fuel replacement. This will be of particular importance as the nation continues to move towards using mobile hydrocarbon fuels with higher ethanol content. These ethene measurements are discussed in light of the potential enhancement of ethene levels expected from the anticipated increases in ethanol use as a renewable biofuel.

2. Experimental methods

Air samples were collected at 261 sites located in New Mexico, Texas, Louisiana, Arkansas, Oklahoma, Kansas, and Mississippi (Fig. 1) from April 28 to May 3, 2002. Sample sites were chosen to be not obviously impacted by local sources of hydrocarbons. Two liter air samples were collected by hand in electropolished stainless-steel evacuated canisters at ground level and shipped to the University of California, Irvine for analysis of ethene and other non-methane hydrocarbons by using GC/FID. Details on this methodology have been described in detail previously (Barletta et al., 2005; Blake et al., 2003). All but one of the samples were taken at a significant distance from any nearby major highways to minimize local source impacts. One sample collected fairly close to a highway was found to have high ethene (2.4 ppb) as well as elevated ethyne (3.9 ppb), benzene (0.4 ppb), and toluene (1.6 ppb) indicating that a significant impact from the highway had occurred. That data point has been removed from the data analysis as it does not represent a regional value. Complete details on the data set are given in Appendix I, including location of sample (longitude and latitude), date and time sampled (CST), and concentrations for ethene, ethyne, benzene, and toluene in ppt.

3. Results

The regional distribution of atmospheric ethene levels observed during this period is shown in Fig. 2 and a frequency distribution of the results is shown in Fig. 3. The time of sampling versus the ethene levels are given in Fig. 4. These samples were collected across the region under a variety of meteorological conditions from

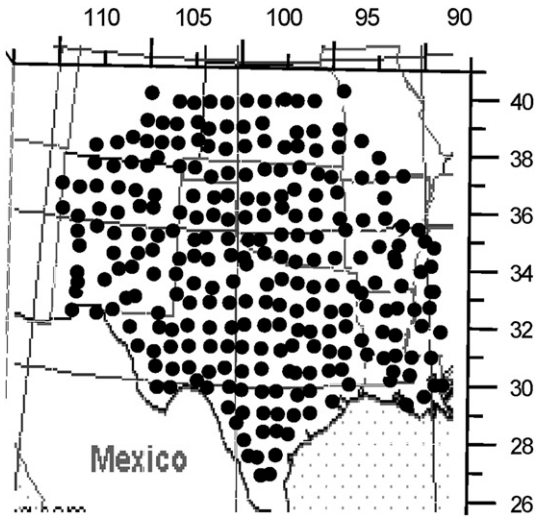

Fig. 1. Location of the 260 sample sites in the southwestern and south central U.S.

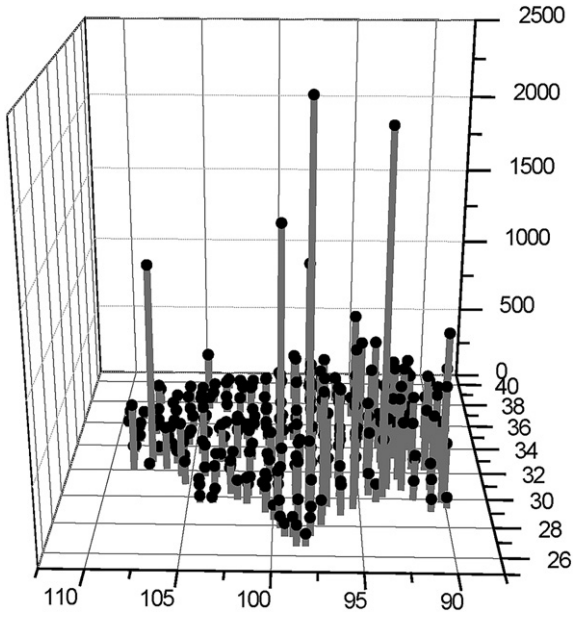

Fig. 2. Atmospheric ethene concentrations (ppt) measured in samples collected from April 28 to May 3, 2002 in the southwestern and south central U.S. Note western data over deserts is lower than eastern values over vegetated area.

calm to windy. An examination of the ethene concentrations as a function of time of day indicates no significant differences between early morning, afternoon, and evening across the entire region (See Fig. 4). Hourly means, minima, and maxima values along with the number of samples taken during each hourly period are shown as a whisker plot in Fig. 4. The hourly means indicate that slightly higher values may have occurred during the early morning and early evening hours, which would be consistent with the anticipated boundary layer increases in ethene emissions from ground-based regional vegetative sources. However, the variance indicates that the ethene levels reported in this data set were not impacted by any significant local ethene sources.

The minimum ethene concentration over all 260 sample sites was observed in New Mexico at 14 parts per trillion (ppt) and the maximum ethene concentration was measured in East Texas at

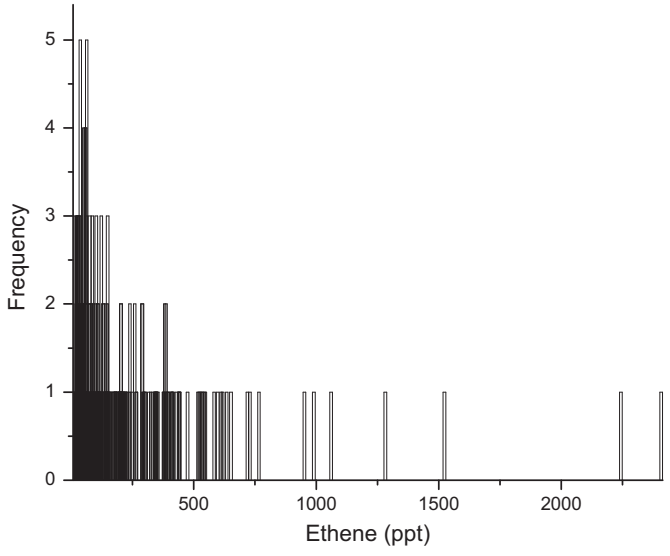

Fig. 3. Frequency distribution of atmospheric ethene concentrations (ppt) observed from April 28 to May 3, 2002 in the southwestern and south central U.S.

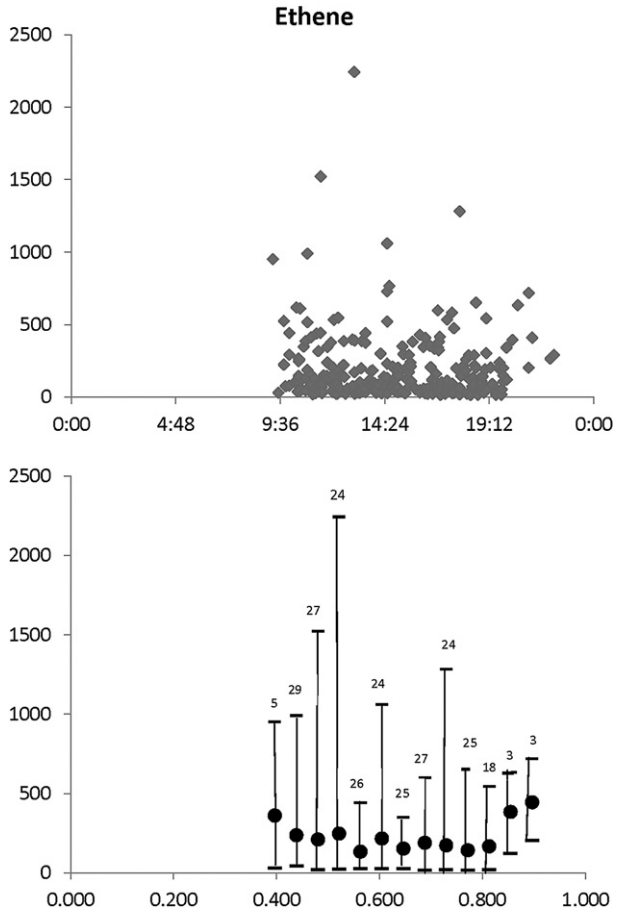

Fig. 4. Ethene values as a function of time sample collected. Times are Central Standard. Samples collected across region from 4/30/2002 to 5/04/2002. Bottom graph are hourly means with minima and maxima noted in whisker plots. Number of samples for each hour are given above the hourly points (see Appendix I.)

2407 ppt (i.e. 2.4 ppb). The mean concentration observed over all sample sites was 204 ppt with a standard deviation of 282 ppt and a median concentration of 112 ppt. Only 5 samples were observed over 1 ppb ethene and these were collected in East Texas (2.4 and 2.2 ppb), West Texas (1.5 ppb), New Mexico (1.3 ppb), and Louisiana (1.1 ppb). Overall, the results show that the background ethene levels over the sampling region were fairly low, in the <1 ppb range.

The observed ethene concentrations are summarized by region in Table 1. The highest overall ethene concentrations were observed in East Texas (mean of 399 ppt), and Louisiana, Arkansas, and Mississippi (mean of 337 ppt). The lowest overall ethene concentrations were observed in New Mexico (mean of 95 ppt). Intermediate overall ethene concentrations were observed in

Table 1
Ethene concentrations (ppt) observed from April 28 to May 3, 2002 in 6 sampling regions in the southwestern and south central U.S.

Region	Number of samples	Mean	Minimum	Maximum
East Texas	44	399	64	2243
West Texas	46	126	17	1523
Kansas	45	117	24	951
Oklahoma	44	137	17	652
LA, AR, MS	42	337	47	1060
New Mexico	39	95	14	1282
Total	260	204	14	2243

West Texas (mean of 126 ppt), Kansas (mean of 117 ppt), and Oklahoma (mean of 137 ppt). This is consistent with ethene being associated with biological sources. Indeed, a comparison of the ethene values shown in (Fig. 2) with vegetation maps for the sample regions (Global Forrest Watch, 2011) indicates that the higher ethene levels (individual and means) observed during the study were found in the regions where the vegetation is most dense. That is, the western portion of the study, which is drier (desert), was found to have lower ethene levels as compared to the more forested eastern study area with higher ethene levels. Thus, a background regional value of 0.1 ppb ethene can be used for desert ecosystems and a value of 0.3 ppb for grass/forest regions based on the data presented here. Other important sources of hydrocarbons across the sampling regions are from natural gas wells, especially in western Texas and Oklahoma, but these are not significant sources of ethene as the ethene levels in natural gas are extremely low (Stahl, 1969; Sawada and Totsuka, 1986).

Past studies have shown that combustion and cracking of hydrocarbons and organics, especially biomass burning, are important sources of ethene (Sawada and Totsuka, 1986). Ethene has also has been found to be produced during in-situ biochar production (Spokas et al., 2010). Ethyne (acetylene) is also produced in combustion of fossil fuels (especially in mobile sources, i.e. internal combustion engines) and fossil fuel sourced ethene has been evaluated by correlations with ethyne levels. Benzene and toluene emissions from gasoline engines are also emitted from incomplete combustion in mobile vehicle sources. Therefore, mobile vehicle sourced ethene is anticipated to correlate with ethyne, benzene, and toluene levels. For example, correlation plots of ethyne and ethene have been used to determine the influence of local and regional sources due to internal combustion engines in Ireland (O'Donaghue and Broderick, 2009). Correlation of ethene versus ethyne, benzene, and toluene are presented in Fig. 5 for the 260 samples collected. Linear correlation fits for ethene versus ethyne had an r^2 of 0.33, while ethene versus benzene gave an r^2 of 0.26. Toluene showed little or no correlation with ethene. These correlations indicate that approximately 70 percent of ethene seen at these sites is due to biogenic sources. These biogenic sources would include natural vegetative emissions as well as biomass burning (natural fires and agricultural burning). The correlations observed are consistent with previous estimates of ethene sources reported in the 1980s where 21% of ethene was apportioned to anthropogenic fossil fuel sources, and 77% was estimated to be from biomass burning (Sawada and Totsuka, 1986). Strong correlations between ethene and ethyne are usually seen where there is a direct impact from combustion sources, such has mobile sourced emissions from highways, (O'Donaghue and Broderick, 2009). The lower correlations reported here for ethene versus ethyne, benzene, and toluene along with no significant trends in the ethene levels as a function of time of day as well as the observed lower levels found in the desert regions in the west compared to the more vegetated eastern sites all indicate that this data set in 2002 is representative of a biogenically sourced regional background for ethene.

Thus, the ethene concentrations observed below 1 ppb accross this region are likely to be a good estimate of the regional background ethene levels that vegetation and agricultural ecosystems are currently being exposed to in the absence of significantly higher ethanol use and biomass burning, which are anticipated to be significant sources of ethene. Indeed, recent biomass burning emission estimates for a wide range of natural biomass materials (e.g. grassland to forest fires) indicate emissions of ethene at approximately one gram per kg of material burned (Akagi et al., 2011; Andreae and Merlet, 2001).

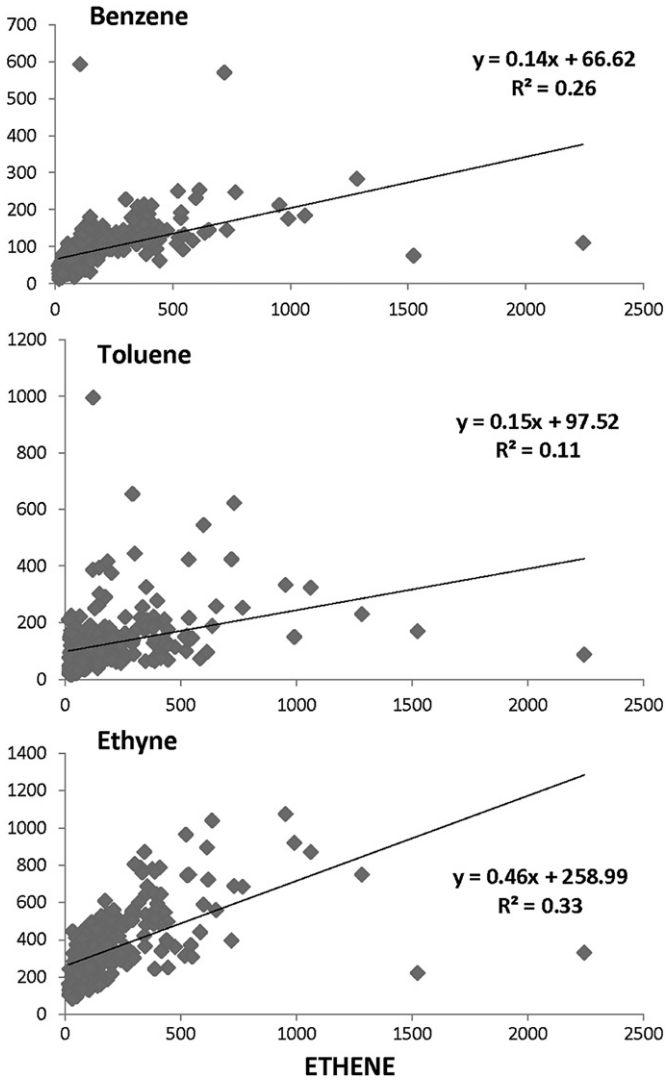

Fig. 5. Linear least squares correlations of atmospheric ethene (*x*-axis) vs benzene, toluene, and ethyne concentrations (ppt) observed in 260 samples collected from April 28 to May 3, 2002 in the southwestern and south central U.S.

4. Discussion

Note that the lifetime of ethene is determined by atmospheric oxidation as it does not undergo photolysis in the troposphere. Ethene is oxidized in the troposphere primarily by OH radical at room temperature with a rate constant of 8.5×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and to a lesser extent by ozone with a rate of 1.75×10^{-18} cm^3 molecule^{-1} s^{-1} at 298 K (Finlayson-Pitts and Pitts, 2000). Both OH and ozone reactions with ethene lead to the formation of formaldehyde and radical species, which can increase the formation of tropospheric ozone through the conversion of NO to NO_2 by peroxyradicals such as HO_2 formed from formaldehyde oxidation and photolysis. In continental air, ethene lifetimes are anticipated to be approximately 1.5–3 days, assuming that OH concentrations are in the range of 0.5 to 1.0×10^6 molecules cm^{-3}. Thus, the production of ethene from combustion including wildfires, agricultural burning, and the use of increased levels of ethanol/gasoline fuel blends will have impacts on regional scales, due to the half-life of about 2 days.

Background measurements of ethene along with few other light alkenes were determined over a season at the Harvard Forest. That

data set was found to have a weak correlation with acetylene measurements suggesting that there was some transport of anthropogenic combustion sourced ethene emissions impacting the site (Goldstein et al., 1996). Measurements of ethylene/acetylene were found to be better correlated in January than in July consistent with a biogenic source of ethene in the spring. The data from that work are consistent with those reported here, i.e. that background levels of ethene are at levels of <1 ppb when the correlation with acetylene was taken into account indicating some anthropogenic contributions impacting the Harvard Forest site. Background levels of ethene as well as measurements made during a forest fire plume event were obtained in Australia by using high resolution FTIR techniques (Rinsland et al., 2005). Again, background ethene levels were found to be less than 1 ppb consistent with the results reported here, while ethene production from the fires led to observations of 37 ppb in the fire plume.

Measurements of ethene in a megacity environment (Mexico City) were found to be at much higher levels than observed in this study. Atmospheric concentrations of ethene were reported in the range of 10–60 ppb in Mexico City with higher levels in the commercial sectors and lower values in residential areas (Altuzar et al., 2001, 2005; Velasco et al., 2007). High levels of biomass combustion have been reported in Mexico City (Marley et al., 2007, 2009). It is anticipated that the high ethene levels observed in this megacity might be similar to levels that could be reached with the anticipated use of higher ethanol/gasoline fuel blends such as E85 during early morning hours when boundary layer heights are at a minimum and maximum emissions are expected (Jacobsen, 2007; Ginnebaugh et al., 2010). The anticipated enhanced ethene emissions from the use of increased ethanol fuel usage could lead to a significant enhancement in ethene exposure to both natural and agricultural vegetation. Studies of wheat and rice production in enclosed structures conducted as preparation for possible lunar food production, found reductions in crop yields of 50% or greater with ethene exposures of 50 ppb (Klassen and Bugbee, 2002).

Additionally, enhanced atmospheric levels of ozone and PAN from higher level ethanol/gasoline blends will be an added stress to ecosystems as these oxidants are also known to be potent plant toxins. The combination of ethene increases with enhanced ozone and PAN as well as increased emissions of NO and aldehydes due to use of higher than current E10 gasoline blends, (i.e. >E30) would likely lead to potential impacts on both natural and agricultural ecosystems that could also have effects on the uptake of carbon dioxide as these pollutants are known to cause senescence and reduce photosynthetic abilities of plants.

Other sources of ethene including biogenic emissions and biomass burning as well as in-situ biochar production (Sawada and Totsuka, 1986; Spokas et al., 2010) are also not well characterized. In addition to ethene increases from combustion of ethanol/gasoline blends, emissions from biomass burning and natural vegetation are also anticipated to increase in the future with increasing climate change. This is due to the projected increases in tropospheric carbon dioxide that act to “fertilize” plant growth. This enhanced plant growth in a warmer climate will likely lead to enhanced emissions of biogenic hydrocarbons including ethene. It will also lead to increases in brush and forest fires as the growth is enhanced by earlier springs and longer growing seasons. As ethene has been determined to be a very potent plant growth hormone and potential carcinogen (Burg and Burg, 1965; Ecker, 1995; Harvey, 1928; Stahl, 1969), it is important that we begin to determine the current baseline levels of ethene in the atmosphere as well as the effects of elevated ethene exposures to both natural and agricultural vegetation in order to insure that this agent does not cause significant impacts on the biosphere as we develop ethanol as a biofuel.

5. Conclusion and recommendations

Background ethene levels in vegetated and agricultural regions in the U.S. are likely to be at the levels measured in this 2002 study, of 0.5 ppb or less, in the absence of significant amounts of biomass burning or enhanced ethanol combustion. Current vegetation and agricultural ecosystems have been acclimated to these levels, noting that ethene is a potent plant growth hormone. Anticipated increases in fuel ethanol content of E30 or greater may lead to higher atmospheric levels of ethene on regional scales. As noted by previous workers (Jacobsen, 2007; Ginnebaugh et al., 2010; Tanner et al., 1988; Gaffney and Marley, 2009), the combustion of ethanol has the potential to increase regional ozone and PAN levels due to the increased emissions of acetaldehyde, ethene, and nitrogen oxides that are tied to the photochemical production of ozone and PAN. Methane releases from ethanol combustion are also likely, noting that it is produced along with ethene and is more resistant to catalytic removal in vehicular exhaust. Emission estimates for the scenario of increasing gasoline blends from E5 to E85 indicate that ethene vehicular emissions will increase by factor of 2–10 times (See: Supplementary Material Table 11 in Ginnebaugh et al., 2010). The emission of ethene is estimated to be strongly dependent on temperature with higher emissions during colder periods (i.e. winter months). The current use of motor vehicle ethanol (E10) in 2010 has risen by a factor of 6.2 since 2002 (United States Energy Information Agency, 2012), and would be expected to increase further if the country moves towards E85 use. Thus, ethanol fuel use is anticipated to increase and with it the emissions of ethene are likely to increase by a factor of 2–10. The emission of ethene will strongly depend upon the exhaust gas catalyst condition and operating conditions with “cold start” emissions being the major issue.

It is clear that there is a need for background determinations of ethene if we are to determine the impacts of potential increases in this key pollutant as we move towards the increased use of biofuels including ethanol/gasoline blends. We would note here that ethene produced from corn-derived ethanol could be distinguished from other sources of ethene by carbon isotopic measurements. Corn, as a C-4 plant, produces ethene with a stable carbon isotopic ratio ($^{13}C/^{12}C$) of approximately 13–14 parts per thousand enriched in ^{13}C than that produced from C-3 plants (Gaffney et al., 1978, 1979). In addition, ethene produced from fossil fuel combustion can be distinguished from that produced by combustion of modern biomass by determination of radiocarbon content. Therefore, by determining the isotopic signature for both stable and radiocarbon, the relative sources of ethene from ethanol use, natural vegetation, biomass burning, and fossil fuel combustion contribution could be evaluated (Marley et al., 2009).

The current trend towards the use of ethanol/gasoline fuel blends with increasing ethanol content requires that the potential impacts of cold start emissions of hydrocarbons such as ethene and methane as well as the enhanced emissions of aldehydes and nitrogen oxides associated with combustion of these fuels be recognized and better evaluated. These primary emissions and their secondary products, ozone and PAN, may cause stress to agricultural and terrestrial ecosystems. Mitigation of these emissions should be considered along with long term baseline monitoring to assure that significant ecosystem damage as well as agricultural and human health impacts are avoided as we seek to develop an environmentally sound sustainable energy practice for biofuels (e.g. ethanol). Ethene measurements should be implemented in regional areas as we continue to increase ethanol use in order to determine the potential exposure levels. While it is well known that ethene is a potent plant growth hormone that is particularly effective on flowering plants (Woltering, 1987), little

quantitative data are available on the chronic effects of low ppb or sub-ppb ethene exposure for most plants and crops. As indicated in this data set, both biomass burning (agriculture and controlled burns as well as wildfires) along with increased use of ethanol fuels anticipated in the future, will likely increase current and future levels of ethene from the estimated past background of 0.1–0.3 ppb to higher levels. This will require continued measurements, modeling efforts, and biological dose/response data to be obtained that is beyond the scope of this current work. Of concern will be both chronic effects on biota due to higher levels, as well as acute impacts from high ethene level plumes from both cities (with enhanced ethanol use) and from natural and agricultural burning plumes that are known to contain tens of ppb levels of ethene.

The emissions of ethene and acetaldehyde anticipated from increased use of ethanol as a motor vehicle fuel will also increase PAN and ozone levels regionally. PAN and ozone are potent plant toxins and are also of concern for human health impacts. They were originally recognized due to their causing chlorosis and leaf damage to numerous plant species including crops (Middleton and Darley, 1961). PAN is known to cause visible damage to a number of plants at 10 ppb, while ozone can stress or damage plants at levels above 40 ppb (Bell and Treshow, 2002). Indeed, there has been some recognition that higher levels of both carbon dioxide and ozone levels will affect crops and crop-yields to the extent that the need for bioengineering crops to withstand these changes may be necessary (Ainsworth et al., 2008). Noting that ethene, PAN, and also ozone increases are likely with the use of ethanol gasoline blends, especially if we move to E85, it is strongly recommended that we look to reduce the ethene, aldehyde, and NOx emissions from the combustion of these fuels. Since much of the organic emissions will primarily occur during cold-start situations or when oxidative catalyst systems are not maintained, the use of hybrid vehicles or other technologies where the emissions can be controlled should be strongly considered.

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Appendix I. Data.

Date	Time	Lat. degrees	Long. degrees	Ethene	Ethyne	Benzene	Toluene
5/2/02	17:29	29.63232	96.89938	583	440	116	74
5/3/02	16:52	29.00057	98.57243	324	786	179	218
5/3/02	10:50	29.47115	95.3656	990	918	176	150
5/3/02	12:14	29.01645	96.09958	176	433	142	72
5/3/02	14:36	28.99498	97.15207	766	684	247	253
5/3/02	15:35	28.95637	97.81443	212	503	122	145
5/2/02	18:27	29.76077	96.0896	135	396	79	60
5/1/02	19:50	31.76662	96.14543	201	532	156	96
5/2/02	10:30	31.22605	96.12338	612	895	253	96
4/28/02	17:40	31.9559	98.56637	199	263	n.a.	n.a.
4/28/02	18:53	32.759	98.49863	143	352	86	262
5/2/02	16:28	30.35917	96.9712	354	686	188	209
4/28/02	14:12	29.71963	98.6783	300	805	228	444
5/1/02	18:50	31.81592	96.75188	110	417	99	70
5/1/02	17:54	31.28588	97.07602	146	419	98	64
4/28/02	16:34	31.1855	98.72122	118	333	94	387
5/2/02	11:45	31.08005	95.1888	346	535	143	65
4/28/02	15:30	30.48472	98.7035	173	446	115	291
4/28/02	*10:33*	*30.3261*	*97.9268*	*2407*	*3687*	*394*	*1589*
4/28/02	12:54	29.73748	97.94323	396	592	189	277
5/2/02	15:01	30.37248	96.11635	182	537	121	416
5/2/02	13:00	30.45062	95.23058	390	559	143	n.a.
4/29/02	10:20	33.3827	97.82495	617	721	n.a.	n.a.
5/1/02	13:38	32.67183	97.77408	108	302	92	78
4/30/02	19:38	32.45878	95.07573	196	340	129	94
4/30/02	17:34	31.9045	94.4398	474	359	144	113
5/1/02	16:53	31.09115	97.75847	381	519	142	221
5/1/02	11:40	32.47423	96.84815	134	354	86	161
5/1/02	10:26	32.67233	96.02862	248	305	101	72
4/30/02	18:17	31.81262	95.09233	122	348	79	106
4/28/02	19:50	33.37317	98.45288	107	391	83	190
4/29/02	12:03	33.2762	96.99318	533	749	177	424
4/29/02	18:07	33.0865	93.5051	259	478	140	162
4/29/02	16:50	33.18302	94.16158	598	588	231	545
5/1/02	14:46	32.01485	97.73793	65	269	75	62
4/29/02	15:12	33.29278	95.08887	349	480	209	326
4/28/02	13:45	33.31093	95.9627	115	296	147	152
4/30/02	12:59	30.37293	93.59723	2243	329	110	88
4/29/02	19:03	32.57197	93.43223	543	370	92	143
4/29/02	19:59	32.48043	94.35303	341	421	175	176
4/30/02	10:26	31.49663	93.47268	266	266	88	79
4/30/02	11:26	31.00278	93.29282	443	249	63	68
4/30/02	15:24	30.4943	94.40183	122	209	83	92
4/30/02	16:10	31.0474	94.38982	345	364	107	175
4/30/02	13:54	30	94	98	240	60	81
4/30/02	13:00	38.75462	99.87157	171	609	108	186
5/3/02	14:00	39.05795	105.091	29	166	31	54
5/2/02	15:00	37.44457	107.8062	162	298	83	125
4/30/02	17:00	38.13162	101.7579	102	243	42	73
5/1/02	17:15	38.2711	104.2754	56	276	54	89
4/30/02	19:20	38.3548	102.3038	90	378	71	101
5/1/02	13:00	38.2793	103.4096	24	155	28	68
5/3/02	9:30	38.26768	106.721	30	218	36	32
5/1/02	19:30	37.74425	104.499	54	275	49	55
4/28/02	15:00	39.80313	99.72103	33	325	63	48
4/28/02	17:00	39.80125	97.76317	31	444	73	48
4/29/02	12:00	38.1825	94.68632	86	459	76	59
5/3/02	12:00	38.32112	105.1112	34	213	34	68
5/2/02	13:20	37.44558	106.8855	36	207	37	75
4/30/02	16:50	38.77712	101.7338	62	403	77	110
5/1/02	10:00	37.41028	102.4461	79	138	24	66
5/1/02	14:00	38.90825	103.4697	81	302	55	84
5/2/02	18:30	38.12468	107.8132	85	190	34	43
4/30/02	9:15	38.9147	97.88305	951	1074	213	333
4/28/02	11:20	39.68593	102.5762	40	323	64	79
4/30/02	12:00	38.06522	99.77098	205	479	95	106
4/30/02	14:30	38.80738	100.7813	117	406	81	175
4/29/02	16:15	38.70583	96.96433	51	366	62	73
4/28/02	9:45	39.81997	104.7743	223	468	98	151
4/30/02	17:50	39.799	96.97518	63	400	54	222
4/28/02	13:15	39.7421	101.692	37	246	39	26
4/29/02	11:00	38.73822	94.69533	155	527	99	152
4/30/02	11:20	38.15518	98.76643	317	597	142	182
4/29/02	18:45	38.11587	97.65242	128	454	70	139
4/29/02	15:00	38.66652	96.10175	142	474	73	44
4/30/02	16:00	38.09088	100.8287	37	320	54	125
4/30/02	17:50	39.01165	102.3536	60	346	60	91
5/1/02	11:30	37.46885	103.3188	27	145	19	90
5/1/02	15:00	38.95477	104.2483	63	275	55	74
5/2/02	9:50	37.43813	105.0367	74	267	44	59
5/2/02	11:00	37.55	105.8944	75	281	49	97
5/3/02	11:00	38.4137	105.83	87	198	47	90
4/28/02	10:30	39.72662	103.35	44	277	50	32
4/28/02	14:00	39.70898	100.7806	59	357	67	34
4/28/02	18:50	39.8268	96.02575	46	409	64	50
4/29/02	9:45	39.66577	94.74948	526	744	125	155
4/28/02	16:00	39.78118	98.72923	47	375	56	55
4/29/02	13:50	38.08103	95.90413	63	373	64	40
4/29/02	17:30	38.18735	96.93353	92	290	38	38
4/30/02	10:00	38.77097	98.87378	293	558	117	138
5/4/02	14:30	30.01265	90.15442	1060	870	184	324
4/28/02	16:00	30.88677	92.42247	429	546	93	211
4/30/02	12:30	37.03768	93.53697	222	510	109	127
4/30/02	15:00	38.3024	93.54928	202	525	100	93
5/1/02	10:00	35.17862	91.74313	442	497	138	176
5/4/02	14:30	30.01265	90.15447	729	689	145	623
5/3/02	19:03	32.60428	89.96025	303	538	114	172
5/3/02	21:00	31.72417	89.87187	718	394	571	425
4/30/02	17:15	34.21137	92.04852	534	748	193	217

5/2/02	13:30	33.97812	89.97947	376	778	214	68
5/3/02	12:00	30.96515	90.71525	153	203	62	61
5/3/02	10:15	30.33668	90.74373	102	185	56	63
5/2/02	18:30	32.58035	91.6283	288	544	138	127
5/1/02	19:40	34.72808	91.54597	238	463	126	69
4/27/02	14:30	30.16297	91.78937	106	306	593	148
4/29/02	14:30	33.45782	92.7633	230	418	92	94
5/3/02	18:35	33.19153	89.76463	202	406	85	154
5/1/02	21:10	35.29962	91.5212	410	483	157	104
5/3/02	13:20	31.98367	90.44623	387	242	80	192
5/2/02	16:15	33.30075	91.54065	408	788	212	97
5/3/02	22:10	30.94193	89.82422	290	327	91	654
5/2/02	21:00	31.01233	91.63373	203	301	97	76
5/1/02	18:30	34.1745	91.67007	219	500	132	63
4/30/02	19:00	37.0847	92.43165	190	382	85	181
5/2/02	12:30	34.59028	89.84907	386	765	182	65
5/1/02	11:15	36.21028	92.49565	438	397	154	133
4/30/02	20:15	36.97713	91.4841	394	643	117	129
4/30/02	16:45	37.77513	92.59708	159	399	81	95
4/29/02	18:00	34.30978	93.5401	216	528	106	115
4/29/02	20:30	35.34388	93.74445	634	1039	138	188
4/29/02	10:50	31.74093	92.5751	517	313	109	149
4/29/02	12:15	32.43183	92.41858	548	307	133	146
4/28/02	11:15	29.33382	90.84513	59	333	75	85
5/1/02	13:30	35.51932	92.45495	441	388	120	122
5/2/02	20:00	31.70473	91.53932	120	444	106	996
5/3/02	15:40	32.52113	90.82653	381	485	114	129
5/3/02	16:30	33.18243	89.63717	206	353	147	84
5/4/02	12:00	29.61487	89.91162	47	93	32	27
5/2/02	14:30	33.73808	90.65895	521	964	251	100
5/2/02	11:00	34.78718	90.34648	412	643	163	75
5/1/02	22:00	35.26155	90.52253	265	507	128	83
5/1/02	15:15	34.64935	92.62358	296	301	115	89
4/30/02	16:55	32.31073	108.6085	416	338	113	136
5/3/02	11:10	35.94693	107.6214	28	201	61	117
4/30/02	16:57	32.33027	107.6614	16	129	38	20
4/28/02	16:15	36.448	104.6136	25	163	51	172
4/28/02	13:05	35.22777	103.6134	31	140	26	132
5/2/02	16:00	34.41377	106.7845	31	175	42	69
5/1/02	17:14	33.01328	103.335	32	149	80	167
5/1/02	18:06	33.66822	103.34	181	185	79	123
5/2/02	13:20	33.94263	105.7731	36	162	43	73
4/29/02	15:20	36.7044	108.7091	26	140	60	226
4/29/02	17:00	36.8418	109.6481	20	147	46	142
4/29/02	10:30	36.5873	105.6448	62	166	66	172
4/28/02	12:11	35.03778	104.4169	21	137	47	95
5/1/02	10:28	32.39698	106.6146	259	362	106	220
4/30/02	11:05	34.65378	108.6393	20	143	47	150
4/30/02	12:35	33.736	108.7473	23	126	48	120
4/28/02	14:00	36.73192	107.764	44	154	52	186
4/30/02	17:50	32.9299	107.5492	1282	750	283	230
4/28/02	19:05	36.04922	105.4036	51	146	46	83
5/2/02	10:30	33.69842	104.5671	61	305	44	n.a
5/1/02	12:34	32.91982	105.5726	30	146	42	99
4/30/02	10:30	35.1663	108.7465	41	161	45	83
5/2/02	12:40	34.41937	105.4547	59	272	70	88
4/29/02	12:10	36.6948	106.5966	41	156	67	150
5/3/02	13:30	35.81613	106.6064	35	211	49	53
4/29/02	19:30	35.67682	108.7742	28	170	52	164
5/2/02	17:00	35.09315	106.7491	48	203	44	20
4/30/02	18:50	33.4871	107.2392	38	146	50	93
4/28/02	17:50	36.00805	104.6842	34	159	45	147
4/28/02	14:15	35.85603	103.2359	25	150	46	161
4/28/02	11:11	35.08047	105.4405	26	154	54	101
4/29/02	18:20	35.9691	109.5988	14	161	48	211
5/3/02	10:23	35.33648	107.7074	38	218	45	45
5/2/02	14:30	33.87698	106.4742	27	176	44	71
5/2/02	11:45	34.44592	104.5664	239	291	115	58
5/1/02	18:47	34.2441	103.2307	50	152	41	97
5/1/02	15:01	32.32218	104.2642	148	222	60	110
5/1/02	11:25	32.84453	106.0331	63	141	41	51
4/30/02	13:45	33.05073	108.7322	76	167	87	131
4/29/02	10:45	36.57517	94.78352	131	457	104	136
4/29/02	16:50	34.932	95.94498	342	871	132	210
4/28/02	15:30	34.27913	95.9361	68	366	76	106
4/28/02	10:50	35.07327	97.75755	187	513	106	130
4/30/02	15:45	37.18948	99.70633	66	331	51	53
4/30/02	17:10	37.26883	100.6898	22	162	39	54
4/30/02	10:40	36.50715	97.15318	348	644	153	186
5/2/02	19:50	36.40505	97.78073	148	451	132	302
5/2/02	14:50	34.9439	99.50462	45	291	57	49
5/1/02	17:30	36.40117	101.4065	25	121	15	15
5/2/02	11:30	34.96513	100.5928	69	302	63	64
4/30/02	19:30	36.45465	102.542	17	163	27	77
5/1/02	12:10	34.3345	102.4068	96	165	33	43
5/2/02	17:50	36.39732	98.71167	19	242	53	36
5/1/02	13:50	34.22032	101.6684	98	232	43	96
4/30/02	14:45	37.2753	98.69543	210	525	135	135
4/30/02	13:50	37.28242	97.85803	185	512	123	144
4/29/02	13:15	37.22457	95.80147	102	423	75	46
5/2/02	16:50	36.3915	99.58253	36	283	53	41
5/2/02	13:45	34.25613	99.73925	179	371	65	72
5/3/02	14:50	34.44947	98.64128	127	352	76	92
5/1/02	11:30	34.90988	102.4216	38	136	23	24
5/2/02	10:45	35.63755	100.6323	45	300	55	45
5/1/02	16:35	35.79458	101.4245	22	146	17	31
5/3/02	13:30	34.9572	98.87255	59	317	64	56
4/29/02	11:55	37.12085	95.10227	114	494	102	132
4/28/02	12:10	34.3479	97.71982	86	433	96	123
4/28/02	17:15	34.33128	94.82135	113	334	83	104
4/29/02	19:15	35.71002	97.01725	203	510	87	148
4/29/02	15:30	35.71022	95.99767	290	551	108	132
4/29/02	14:30	36.48167	95.908	131	454	82	133
4/28/02	13:45	34.19385	96.95102	73	407	87	120
4/29/02	18:15	35.00047	96.9156	288	503	145	149
4/30/02	11:55	37.23485	96.9156	378	654	161	182
4/28/02	18:35	35.00167	94.64562	652	559	145	258
4/28/02	19:40	35.64122	94.67663	208	558	93	146
4/30/02	18:10	37.12877	101.592	22	150	26	26
5/1/02	10:30	35.6732	102.333	49	156	25	37
5/1/02	14:45	34.98405	101.83	81	155	18	33
5/1/02	18:25	36.4477	100.6582	73	163	29	37
5/3/02	11:45	35.76485	98.68528	122	365	72	72
5/3/02	10:45	35.87085	97.79847	387	512	114	140
5/2/02	15:50	35.72482	99.69902	51	277	48	34
5/2/02	12:20	34.39163	100.4301	60	297	56	50
5/3/02	16:41	31.80165	105.642	333	759	171	255
5/3/02	15:11	31.85002	104.2278	36	119	48	20
5/2/02	18:56	32.73282	100.4543	61	190	76	65
5/3/02	13:03	31.93442	102.7183	28	135	62	52
5/3/02	11:44	31.84932	101.5024	147	251	170	121
5/3/02	10:23	31.88297	100.3207	90	229	78	68
5/3/02	14:21	31.75502	103.5149	141	152	71	40
5/2/02	12:22	33.45705	100.2848	148	193	32	56
4/28/02	15:08	30.52283	104.397	36	106	26	98
4/28/02	16:22	29.80967	104.3109	24	122	45	100
4/28/02	11:09	31.20763	105.3334	128	168	36	250
5/2/02	14:05	33.24192	101.4022	86	209	72	75
5/2/02	15:34	33.32435	102.3439	239	323	93	119
4/29/02	10:27	31.18465	103.5676	101	129	29	110
4/28/02	13:14	31.03245	104.4984	29	81	24	46
5/2/02	10:22	32.79677	99.59153	93	212	65	54
5/2/02	11:27	33.46168	99.66342	1523	220	76	170
5/2/02	16:43	32.70617	102.5919	74	192	68	57
4/28/02	18:40	29.79953	103.5759	17	100	12	46
5/2/02	17:50	32.75613	101.5392	60	192	63	44
4/28/02	19:45	30.43302	103.475	17	107	19	27
4/29/02	12:09	31.2194	102.6158	109	179	85	159
5/1/02	10:27	28.2848	97.2418	141	330	144	52
5/1/02	16:10	30.38327	99.7221	57	171	60	54
4/29/02	17:35	31.23302	101.4573	29	163	59	73
4/30/02	10:26	29.85177	100.4059	145	175	86	394
4/29/02	13:18	30.48563	102.5457	198	267	116	376
4/29/02	18:43	31.24842	100.5262	51	197	75	57
5/1/02	12:32	28.3463	98.55247	138	266	121	156
5/1/02	17:24	31.22412	99.73852	42	168	45	47
5/1/02	15:23	29.7486	99.73713	200	216	94	69
5/1/02	18:57	31.99542	99.62693	30	82	28	36
5/1/02	14:25	28.97373	99.64365	74	183	105	81
5/1/02	11:31	28.37453	97.82032	91	299	113	62
4/29/02	15:01	29.8104	101.5671	147	298	181	131
4/29/02	14:17	30.05383	102.1167	108	255	135	89
4/29/02	19:46	30.50605	100.6631	53	280	108	71
4/29/02	16:21	30.34698	101.5085	56	235	98	106
4/30/02	17:33	26.88097	98.12632	56	209	68	32
4/30/02	13:54	28.02995	99.55343	56	146	61	70

(*continued on next page*)

(*continued*)

Date	Time	Lat. degrees	Long. degrees	Ethene	Ethyne	Benzene	Toluene
4/30/02	15:00	27.50068	99.30142	63	139	63	65
4/30/02	16:43	26.85358	98.62732	112	253	130	122
4/30/02	18:50	27.53807	97.8662	97	132	42	99
4/30/02	12:55	28.62238	99.97667	75	135	93	61
4/30/02	11:35	29.14688	100.4412	150	158	62	97
4/30/02	15:36	27.45925	98.83758	109	251	107	107

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